Transition Metal-Free Cycloamination of Prenyl Carbamates and Ureas Promoted by Aryldiazonium Salts

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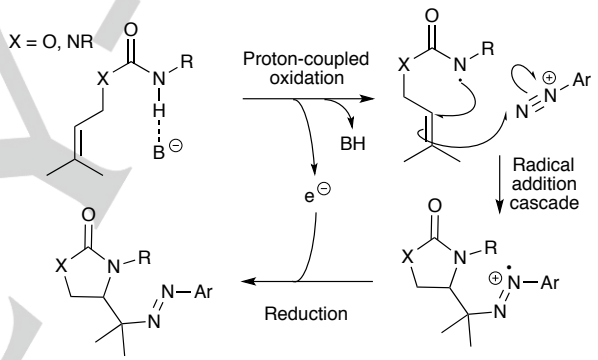
Abstract: On treatment with aryldiazonium salts, prenyl carbamates and ureas undergo redox-neutral azocycloamination. *N*-Aryl *O*-prenyl carbamates in general cyclize in a photocatalytic reaction with visible light and an organic dye. With electron-deficient diazonium salts, electronic matching with an electron-rich *N*-aryl substituent the reaction to proceed in the ground state, without light or photocatalyst. Cyclic voltammetry suggests that this radical reaction is initiated by hydrogen atom abstraction mediated by an aryl radical, followed by a radical addition cascade and proton-coupled hole propagation. The reaction proceeds at room temperature in short reaction times, and a range of functional groups is tolerated.

Amination of olefins is an attractive approach to aliphatic polyfunctionalized molecules, with allylic alcohols and allylic amines being either feedstock chemicals or easily accessible synthetically.[1] Intramolecular cyclization of carbamates and ureas onto a pendent olefin is a convenient way of ensuring selectivity. For example, treatment of allyl carbamates and ureas with electrophilic halogen sources leads to regioselective aminohalogenation of the olefin via a halonium intermediate.[2] However, this approach is limited both by the lack of reactivity, and by elimination side-reactions during functional group interconversions of the halide substituents. Some of these issues may be avoided using metal catalysts. Pd-catalyzed carboamination of allyl carbamates and ureas, using aryl halides as oxidants to form a palladium(II) species, promotes olefin insertion into the amine-metal bond, followed by reductive elimination to the arylated product.[3] Hypervalent iodine oxidants widen the scope of this useful transformation, and enable the formation of two heteroatom-carbon bonds, resulting in aminoalkoxylation or aminofluorination of the pendent olefin.[4]

Following Nicolaou's IBX-mediated intramolecular hydroaminations of allyl carbamates,[5] advances in aminofluorination reactions revealed a new mechanistic approach to the difunctionalization of these substrates. Formation of an *N*-centred amidyl radical allows 5-*exo*-*trig* cyclisation to an intermediate nucleophilic radical whose reaction with fluorine atom donors provides aminofluorinated products.[6] As an extension of this work, copper-mediated diamination reactions exhibit interesting mechanistic behavior, at the interface between free-radical chemistry and more standard polar aminometalation.[7] Unfortunately, these reactions generally rely on expensive or synthetically remote electrophilic amination reagents such as NFSI, *O*-acylhydroxylamines or the Zhdankin reagent, which simultaneously act as two-electron oxidants.

Knowles has shown that proton-coupled electron transfer enables oxidation of amides, carbamates and ureas to electrophilic *N*-centered radicals. A weakly basic but strongly hydrogen-bonding additive significantly lowers the oxidation potential of the substrate, permitting the use of milder oxidants such as excited-state iridium photocatalysts. However, this approach was only applicable to hydro- or carbocycloamination reactions when the intermediate nucleophilic radical was trapped by hydrogen atom donors or electron-deficient olefins.[8]



Scheme 1. Mechanistic rationale for the redox-neutral diamination of allyl carbamates and ureas with diazonium salts.

In this paper we show that diazonium salts constitute a class of reagents capable of trapping such intermediate radicals to form a new C–N bond (Scheme 1). Diazotization of anilines is straightforward under either aqueous or anhydrous conditions, making diazonium salts far more accessible than any other electrophilic amination reagent. Most diazonium tetrafluoroborate salts are stable crystalline solids, indefinitely stable in the fridge. Although free-radical addition onto diazonium salts has been known for over 30 years, their full potential as electrophilic amination reagents has been revealed only recently. Their reduction requires only mild temperatures, in the presence of nucleophilic bases, visible-light irradiation, or weak reductants such as DABSO, and could initiate radical reactions forming intermediates which would ultimately be trapped by an additional equivalent of diazonium salt, terminating the reaction.[9]

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Table 1. Initial investigations using carbamates

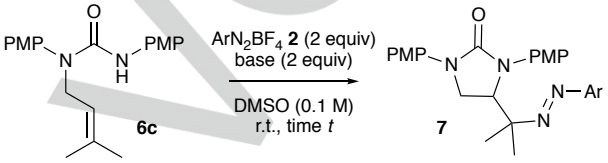
Entry	Substrate	*x* mol% 4DPAIPN	Ar^2	Product, yield / % [a]
1	**1a**	6	*p*-$CH_3OC_6H_4$	**3**, 74%
2	**1a**	0[b]	*p*-$CH_3OC_6H_4$	**3**, 47%
3	**1a**	0, in the dark[b,c]	*p*-$CH_3OC_6H_4$	**3,** <10%
4	**1a**	6	*p*-$CF_3C_6H_4$	**4**, 62%
5	**1a**	0[b]	*p*-$CF_3C_6H_4$	**4**, 69%
6	**1a**	0, in the dark[b,c]	*p*-$CF_3C_6H_4$	**4**, 38%
7	**1b**	3	*p*-FC_6H_4	**5**, (57%)[e]
8	**1b**	0, in the dark, DMSO[b-d]	*p*-FC_6H_4	**5**, (75%)[e]
9	**Urea 6c**	3	*p*-FC_6H_4	No product
10	**Urea 6c**	0, in the dark, DMSO[b-d]	*p*-FC_6H_4	**7b**, 75%

[a] Reactions performed on 0.1 or 0.2 mmol scale (see supporting information). Yields of isolated products. [b]No photocatalyst added. [c]No irradiation. [d]DMSO as solvent instead of CH_2Cl_2. [e]Yields in brackets are spectroscopic yields determined by ^{19}F NMR using trifluorotoluene as internal standard. 4DPAIPN = 1,3-dicyano-2,4,5,6-tetrakis(*N*,*N*-diphenylamino)benzene.[10]

We began our study by submitting *N*-phenyl *O*-prenyl carbamate **1a** to Knowles' photoredox catalysis conditions, in the presence of a diazonium salt. Neutral organic dyes 4CzIPN (1,3-dicyano-2,4,5,6-tetrakis(carbazole)-benzene) and 4DPAIPN (1,3-dicyano-2,4,5,6-tetrakis(*N*,*N*-diphenylamino)-benzene) were used as cheaper alternatives to iridium photocatalysts.[10] Upon irradiation with blue LED, **1a** and diazonium salt **2a** gave the coupling product **3** in 74% and 47% yield in the presence and absence of photocatalyst, respectively (Table 1, entries 1 and 2). There was almost no conversion in the dark and in the absence of photocatalyst (entry 3). This shows that a purely photoinduced reaction between the two substrates, without intervention of 4DPAIPN as redox mediator, is operative to some extent.

Very different results were obtained using the electron-deficient diazonium salt **2c**. Although best yields of product **4** were obtained on irradiation, with or without the photocatalyst (entries 4-6), significant background reaction occurred even in the dark. To further investigate this peculiar behavior, we used electron-rich carbamate **1b** in combination with an electron-neutral diazonium salt **2b** and obtained the expected product **5** in 57% spectroscopic yield under photocatalytic conditions (entry 7). Switching the solvent to DMSO and performing the reaction in the dark in the absence of photocatalyst gave **5** in an improved 75% spectroscopic yield (entry 8). This led to the conclusion that diazonium salts which are more electron-deficient than the substrate promote direct oxidation or hydrogen atom abstraction of **1a** or **1b** even in the ground state. We then evaluated both sets of conditions using the related prenyl-substituted urea **6c**. Photocatalytic conditions in CH_2Cl_2 resulted in low conversion without formation of the expected product **7b** (entry 9). In stark contrast, a 75% yield was obtained in DMSO in the dark (entry 10). This unprecedented reactivity, apparently arising from the interaction of the prenyl urea and the diazonium salt in their electronic ground states, is remarkable, so we turned to exploiting its generality.[11]

Table 2. Optimisation of the reaction conditions using urea substrates



Entry	Ar	Base	*t*	Product, yield / %[a]
1	*p*-$CH_3OC_6H_4$	$(NBu_4)PO_2(OBu)_2$	17 h	**7a**, < 30%
2	*p*-FC_6H_4	$(NBu_4)PO_2(OBu)_2$	17 h	**7b**, 75%
3	*p*-$CF_3C_6H_4$	$(NBu_4)PO_2(OBu)_2$	2 h	**7c**, 77%
4	*p*-$CF_3C_6H_4$	$LiPO_2(OBu)_2$	30 min	**7c**, 84%
5	***p*-$CF_3C_6H_4$**	**$NaPO_2(OBu)_2$**	**30 min**	**7c**, **84%**
6	*p*-$CF_3C_6H_4$	$KPO_2(OBu)_2$	30 min	**7c**, 75%
7	*p*-$CF_3C_6H_4$	Li_3PO_4	17 h	**7c**, 72%
8	*p*-$CF_3C_6H_4$	Na_3PO_4	17 h	**7c**, 56%
9	***p*-$CF_3C_6H_4$**	**$NaPO_2(OBu)_2$**	**15 min**	**7c, 83%[b]**
10	*p*-$CF_3C_6H_4$[c]	$NaPO_2(OBu)_2$[c]	30 min	**7c**, 67%

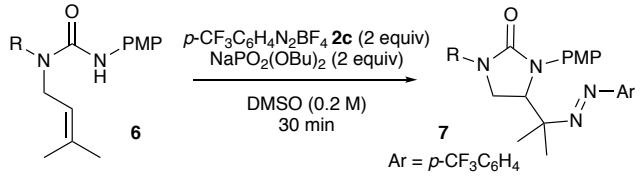
[a]Isolated yield from reaction of **6c** (0.1 mmol, 34 mg), diazonium salt (2 equiv., 0.2 mmol) and base (2 equiv., 0.2 mmol) under nitrogen in dry, degassed DMSO (0.1 M, 1 mL). [b]Reaction carried out with starting material at 0.2 M concentration. [c]1.5 equiv. PMP = *p*-methoxyphenyl.

Upon treatment of **6c** with **2a**, ^1H NMR gave evidence that the triamine derivative **7a** was formed (Table 2, entry 1), but only in low yield even after 17 h. More electron-deficient partners **2b** and **2c** coupled more successfully (entries 2 and 3). Screening a series of bases (entries 4-8) established that the more soluble sodium dibutylphosphate was optimal, and allowed the reaction to be run at greater concentration. Full conversion of **2c** to **7c** was achieved in only 15 min (83% isolated yield, entry 9). Reducing the amounts of diazonium salt and base below 2 equiv. led to lower, but still synthetically useful, yields (entry 10). Commercially available lithium phosphate is a more readily available and scalable alternative (entry 7).

Having identified the optimal conditions for this redox-neutral azocycloamination reaction, we explored its scope (Table 3). Variation of the *N*-substituent of the *N*-aryl urea

showed that a range of *para*- and *meta*-, but not *ortho*-substituents, were well tolerated (**7c-n**).[12] Halo-substituted substrates gave the products **7f-h** in good yields, as did nitriles, esters and acetamides (**7k, l, n**), and the medicinally important trifluoromethoxy group of **7j**.

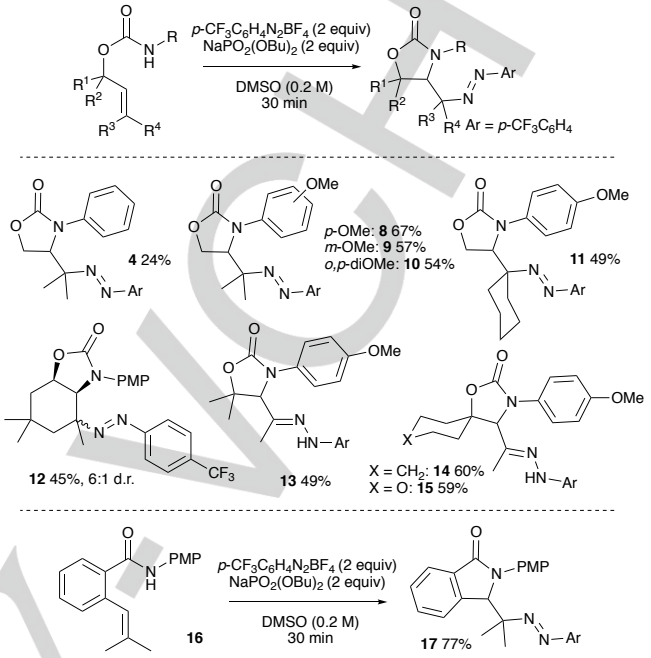
Table 3. Substrate scope of the diamination of ureas.



Entry	Starting material, R	Product, yield / %[a]
1	**6c**, *p*-$CH_3OC_6H_4$	**7c**, 83%
2	**6d**, C_6H_5	**7d**, 76%
3	**6e**, *m*-$CH_3C_6H_4$	**7e**, 87%
4	**6f**, *p*-FC_6H_4	**7f**, 57%
5	**6g**, *p*-ClC_6H_4	**7g**, 80%
6	**6h**, *p*-BrC_6H_4	**7h**, 76%
7	**6i**, *p*-$CH_3SC_6H_4$	**7i**, 65%
8	**6j**, *p*-$CF_3OC_6H_4$	**7j**, 62%
9	**6k**, *m*-$^tBuO_2CC_6H_4$	**7k**, 59%
10	**6l**, *p*-NCC_6H_4	**7l**, 78%
11	**6m**, *m*,*m'*-di$CH_3OC_6H_3$	**7m**, 67%
12	**6n**, *p*-$AcNHC_6H_4$	**7n**, 72%
13	**6o**, benzyl	**7o**, 61%
14	**6p**, *n*-butyl	**7p**, 62%
15	**6q**, cyclopropyl	**7q**, 56%

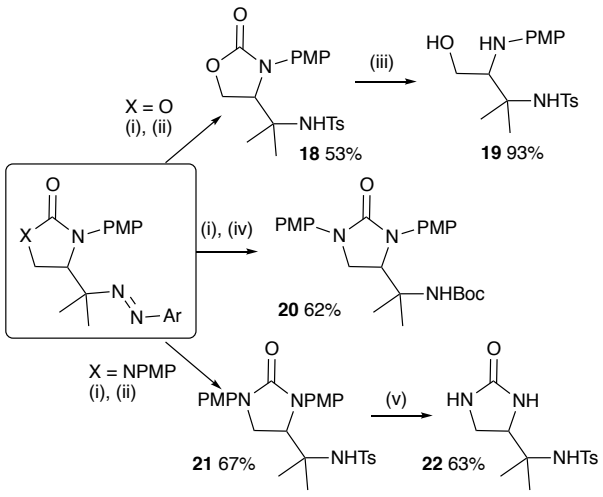
Isolated yield from reaction of **6** (1 equiv., 0.2 mmol), *p*-trifluoromethylphenyl diazonium tetrafluoroborate **2c** (2 equiv., 0.4 mmol, 104 mg) and base (2 equiv., 0.4 mmol, 93 mg) under nitrogen in dry, degassed DMSO (0.2 M, 1 mL). PMP = *p*-methoxyphenyl.

N-Alkyl ureas were likewise cyclized successfully to the triamine derivatives **7o-q**, though yields were slightly lower, and the products were acid-sensitive. Azocycloamination of carbamates allows the use of allylic alcohols as precursors of diamino alcohol derivatives, and a series of *N*-aryl *O*-prenyl carbamates **1** were made and treated under the same reaction conditions (Scheme 2). These carbamates also cyclized successfully to products **4**, **8**, **9** and **10**, with the best yields being obtained from substrates with electron-rich *N*-substituents. Cyclohexane-containing products **11** and **12** could be obtained in moderate yields. Among mono- and disubstituted alkenes, only *α,α*-disubstituted crotyl carbamates gave a product, as a mixture of isomers. These isomerised to the single hydrazones **13-15** in acid. The carbamate linkage was not essential: easily accessible 2-alkenyl benzamide **16** gave isoindolinone **17** in good yield.[13]



Scheme 2. Extended substrate scope of the diamination. Yields of isolated products. PMP = *p*-methoxyphenyl.

Deprotection of the acid-sensitive products required stepwise partial neutral reduction to the hydrazine followed by hydrazine cleavage with acid (Scheme 3). **18**, **20** and **21** were isolated after a Boc- or Ts-protection. Basic hydrolysis of **18** gave the diamino-alcohol **19**; CAN-mediated deprotection of **21** gave the urea **22**.



Scheme 3. Deprotection of the products, see supporting information for details. (i) Pd/C, H_2, MeOH, then HCl_{aq}; (ii) NEt_3, TsCl, DCM; (iii) NaOH, EtOH; (iv) K_2CO_3, Boc_2O, DCM/H_2O; (v) cerium ammonium nitrate, MeCN/H_2O. PMP = *p*-methoxyphenyl.

The mechanism of the reaction was investigated using the reaction between **6c** and **2c** as a model (see full details in the supplementary information). When the reaction in Table 3 entry 1 was performed in the presence of 2 equiv. 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), the only product was 1-(2,2,6,6-tetramethylpiperidinyloxy)-4-trifluoromethylbenzene, even in the absence of **6c**. When dissolved in moist DMSO-d_6, **2c** slowly and cleanly decomposed to 4-trifluoromethylphenol over 48 h. In contrast, with $NaPO_2(OBu)_2$, there was significant decomposition of **2c** to trifluorotoluene and its derivatives, with only small amounts of 4-trifluoromethylphenol, within 3 h. This reaction occurred even more rapidly in the presence of a urea lacking an alkene (1,3-bis(4-methoxyphenyl)-1-methylurea: see supporting information). These experiments are consistent with the initiation step of the reaction being base-mediated decomposition of **2c** to the corresponding aryl radical, with the diazonium salt and/or the aryl radical interacting with the urea, by electron transfer, hydrogen atom abstraction or charge transfer.

Cyclic voltammetry in DMSO using Bu_4NPF_6 as electrolyte revealed that $NaPO_2(OBu)_2$ is not redox active within the solvent's electrolysis range, and diazonium salt **2c** has a reduction potential of –0.33 V vs Ag^+/Ag (0.170 V open circuit potential) which does not change upon addition of base. The urea starting material **6c** has an oxidation potential of 1.21 V, decreasing to 1.06 V in the presence of 3.8 equivalents of base, in line with Knowles' previous reports.[8]

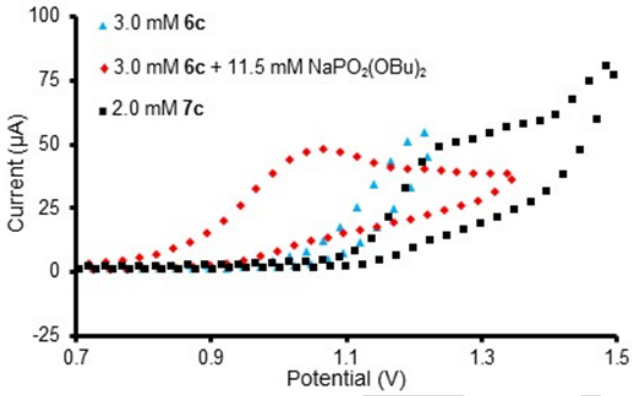
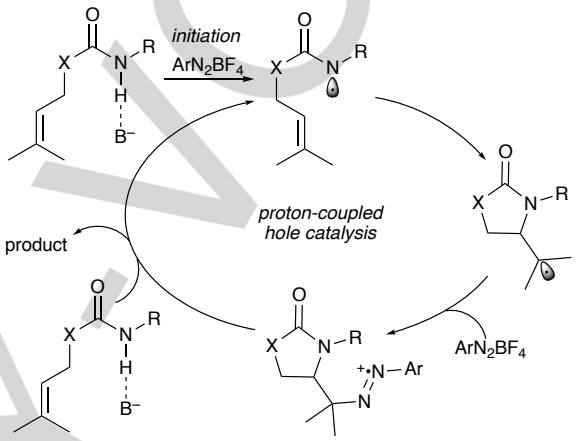


Figure 1. Overlaid cyclic voltammograms of **6c** (▲, 3.0 mM), a mixture of **6c** and $NaPO_2(OBu)_2$ (♦, 3.0 mM and 11.5 mM respectively) and **7c** (■, 2.0 mM) in DMSO containing 0.1 M NBu_4PF_6. Ag reference electrode, glassy carbon working electrode, Pt mesh counter electrode were used. Scan rate: 0.1 V/s.

Oxidation of **6c** by **2c** is therefore thermodynamically unfavorable in the ground state, even in the presence of base. Additionally, the fact that the reaction proceeds in the dark, in a highly polar and dissociating solvent, further suggests a ground state reactivity.[14] We therefore propose that the reaction is initiated by decomposition of **2c** to an aryl radical, which abstracts a hydrogen atom from **6c**.[15] Electron-deficient diazonium salts decompose simply in the presence of base,[9f] while electron-rich diazonium salts require additional activation by light.[16]

Radical addition of an amidyl radical onto an olefin, and radical addition of a tertiary alkyl radical onto a diazonium ion are both precedented, as discussed above. Remarkably, cyclic voltammetry experiments showed that product **7c** has a first oxidation potential of 1.26 V, which is higher than that of **6c** in the absence or presence of base. Thus, 'hole catalysis' appears to be responsible for the propagation of the reaction: a radical cation intermediate resulting from the addition onto **2c** oxidizes a molecule of **6c** to generate the product and an amidyl radical intermediate ready for cyclization.[17] We therefore propose that the reaction follows the mechanism depicted in Scheme 4.



Scheme 4. Proposed reaction mechanism

In conclusion, the use of diazonium salts as both oxidants and radical acceptors leads to a new transition metal-free azocycloamination reaction of prenyl carbamates and ureas by intramolecular radical attack of an amidyl radical on an alkene. The diamination tolerates a range of functional groups, and generally proceeds in high yields, provided the amidyl radical bears an *N*-*p*-methoxyphenyl substituent. The reaction is atom-efficient and easy to perform, and the products are obtained in short reaction times under concentrated conditions. Cyclic voltammetry identified a likely reaction mechanism involving proton-coupled hole catalysis, with a visible light-promoted diamination reaction providing an alternative method for otherwise unreactive substrates. Further ground state electron-transfer promoted reactions involving ureas are under investigation and will be reported in due course.

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Keywords: amination • carbamate • diazonium salt • radical chemistry • urea

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[13] A diastereoselective cyclisation was achieved using a sulfinamide auxiliary: see supporting information..

[14] The formation of a charge-transfer complex was difficult to investigate by UV-Vis spectroscopy due to the formation of highly colored unidentified decomposition products derived from **2c**.

[15] *N*-aryl amides and benzene have similar bond dissociations free energy (BDFE ~ 100 kcal.mol^{-1}). a) J. P. Cheng, Y. Y. Zhao, *Tetrahedron* **1933**, *49*, 5267; b) S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2002**, *36*, 255.

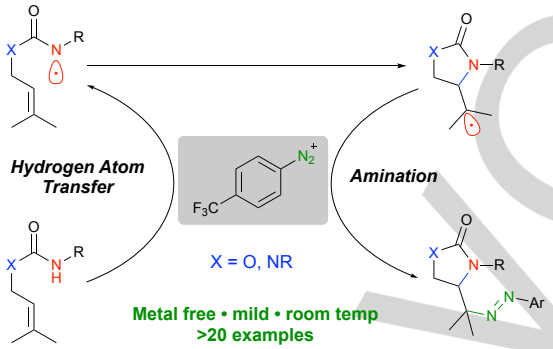
[16] Y. Liu, J.-L. Zhang, R.-J. Song, J.-H. Li, *Eur. J. Org. Chem.* **2014**, 1177.

[17] a) A. Studer, D. P. Curran, *Nat. Chem.* **2014**, *6*, 765; b) L. Pitzer, F. Sandfort, F. Strieth-Kalthoff, F. Glorius, *J. Am. Chem. Soc.* **2017**, *139*, 13652.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

Arenediazonium salts promote the azocycloamination of prenyl carbamates and ureas by acting both as oxidant and radical trap in a mild, metal-free and redox-neutral cascade sequence.



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